2.3. Photodetachment

2.3.1. Introduction

Many important atomic and molecular species exhibit a positive binding energy for an extra electron and are therefore able to attach an electron to form a free negative ion. These ions have been observed and studied from the earliest days of gaseous electronics and mass spectroscopy. Because the binding is due to polarization and exchange forces rather than Coulombic forces, the binding energies are rather small. For example, the binding energy of an electron to neutral atomic hydrogen (electron affinity of H), calculated by Bethe\textsuperscript{1} in 1929 and by Hylleraas\textsuperscript{2} in 1930, is about 0.75 eV. An extensive literature\textsuperscript{3} exists on the use of chemical energy balances and collision energetics for measuring the binding energies of negative ions. Notably successful only for the halogen negative ions, these methods showed that these binding energies range from about 3.1 eV for iodine to about 3.8 eV for chlorine.

The small values of these binding energies imply that the optical spectra of negative ions have particularly interesting characteristics. Some negative ions exhibit absorption continua in the visible or even in the infrared region of the spectrum. Any discrete electronic spectra of negative ions would correspond to a few electron volts at most. However, for many decades the spectra of negative ions remained totally unknown. Conventional optical spectroscopic techniques yielded nothing that could be attributed with any confidence to the electronic transitions in negative ions.

In 1939, Wildt\textsuperscript{4} provided a tremendous stimulus that finally led to observation in the laboratory of optical absorption by negative ions. Wildt, in attempting to explain the solar continuum in the visible spectrum in terms of the opacity of the photosphere, suggested that the atomic process responsible might be photodetachment of the hydrogen negative ion:

\[ \text{H}^- + hv \rightarrow \text{H} + e^- \] (2.3.1)

This interpretation was confirmed by Chandrasekhar and his collaborators\textsuperscript{5} during the early 1940's through a series of calculations of the H\textsuperscript{-} absorption coefficient and its dependence on wavelength. Thus, the spectral properties of a negative ion were shown to have great astrophysical significance, and

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\textsuperscript{1} H. A. Bethe, \textit{Z. Physik} 57, 815 (1929).
\textsuperscript{2} E. A. Hylleraas, \textit{Z. Physik} 63, 291 (1930).
\textsuperscript{4} R. Wildt, \textit{Astrophys. J.} 89, 295 (1939).
\textsuperscript{5} S. Chandrasekhar, \textit{Astrophys. J.} 100, 176 (1944); 128, 114 (1958).

\footnote{† Contribution of National Bureau of Standards, not subject to copyright.}
\footnote{∗ Chapter 2.3. is by Stephen J. Smith.}
the rush was on to develop laboratory techniques for the study of negative-ion spectra.

In 1951, Lochte-Holtgreven\textsuperscript{6} reported the first observation of a continuous emission spectrum attributable to a negative ion. He used a high-current arc discharge in hydrogen and attributed a significant fraction of the observed continuum to the radiative attachment process:

\[ H + e \rightarrow H^- + \nu. \]  \hspace{1cm} (2.3.2)

Attempts to observe negative-ion absorption spectra in ordinary gas discharges have not succeeded. The reason is apparent when one considers that the absorption cross section of a negative ion for photons is perhaps \(10^{-17}\) cm\(^2\), and that the integral of ion density over an optical path must be, therefore, at least \(10^{15}\) ions/cm\(^3\) before conventional absorption spectroscopy becomes feasible. Negative and positive ion densities in a discharge are typically of the order of \(10^8\) ions/cm\(^3\) (Massey\textsuperscript{7}), orders of magnitude too small to produce a measurable attenuation in transmitted photon flux for practical optical path lengths.

In 1954, Branscomb and Fite\textsuperscript{8} introduced an ingenious crossed-beam technique for studying absorption by negative ions, based on the detection of the free electron produced in the photodetachment process [Eq. (2.3.1)]. By this technique, the detachment signal is seen, not as a minute diminution in a photon flux, but as a minute separated electron current, which, nevertheless, can be measured within the limitations imposed by statistical fluctuations. Branscomb and his collaborators have used this technique to obtain definitive information about a number of negative ions, including the electron affinities and cross sections of atomic oxygen,\textsuperscript{9} atomic iodine,\textsuperscript{10} atomic carbon,\textsuperscript{11} atomic sulphur,\textsuperscript{12} and the hydroxyl molecule OH (Branscomb\textsuperscript{13}), as well as the energy dependences of \(H^-\) (Smith and Burch\textsuperscript{14}), \(O^-\) (Smith\textsuperscript{15}), and \(O_2^-\) (Burch \textit{et al.}\textsuperscript{16}).


The crossed-beam method has certain limitations. The optical resolution is not so good as in conventional spectroscopy. The production of negative-ion beams is largely an art, and a limited number of ion species can be produced in quantity. For molecular ions, there is a lack of control over the distribution in electronic and vibrational states. For the case of most atomic ions, the question of distribution over states is probably irrelevant; the ions are presumed to have only one bound electronic configuration, so that all detachments are from the ground state and all transitions result in detachment. Usually, only one term of the ground state configuration is expected to be bound. This situation is discussed in a recent review.\footnote{L. M. Branscomb, in "Atomic and Molecular Processes" (D. R. Bates, ed.), p. 100. Academic Press, New York, 1962.}

The limitations on spectral resolution, to be discussed in more detail in a later section, arise because of the necessity of using a very intense photon beam to produce a measurable photodetachment signal. Thus, for many years, photodetachment work was carried out using sets of broadband, sharp-cutoff filters; and resolution was in the range from 300 to 700 Å. More recently, intense light sources have been used in conjunction with a specially designed, high-aperture monochromator yielding resolutions as good as 20 Å. Near threshold, an elaborate unfolding process has yielded better effective resolution, $\sim 3$ Å.

In 1961, Berry \textit{et al.}\footnote{R. S. Berry, C. W. Reimann, and G. N. Spiro, \textit{J. Chem. Phys.} 35, 2237 (1961).} obtained the first "conventional" photographic negative-ion absorption spectra in a shock tube by loading the hot gas behind a shock front with vaporized alkali halides. The shock contained negative-ion densities of the order of $10^{15}$ ions/cm$^3$, and a multiple-pass optical system was used to obtain the path length needed for good contrast.

Berry has applied the absorption technique to the study of details of the halogen photodetachment cross sections near threshold. These details have not been directly accessible with other methods. However, his method is not so reliable as the crossed-beam method for determining the overall energy dependence of a cross section. The shock-tube method has been used in absorption to determine accurate values of the electron affinities of the halogens and in emission to determine the electron affinity of atomic oxygen.

There have been a number of other exciting advances during the past few years based on the beam, arc, and shock-tube techniques. This chapter will emphasize the recent developments in technique.

2.3.2. The Crossed-Beam Method

2.3.2.1. General Description. The crossed-beam method of studying photodetachment is illustrated schematically in Fig. 1. A beam of negative
ions in high vacuum is crossed by a beam of photons, and the current of free electrons produced at the region of intersection of the two beams is taken as a measure of the rate of absorption of photons by the ions:

\[ X^- + h\nu \rightarrow X + e. \] (2.3.3)

The ions, obtained by extraction through the anode of a gas discharge, are selected by magnetic or by a combination of magnetic and electrostatic analysis, and are focused through the interaction region into a Faraday cage or an open electron multiplier that is used to monitor ion-beam current. Light from an intense arc lamp or a flash tube may be focused through a monochromatizing device into the reaction region. Some sort of radiometric device is necessary to monitor the intensity of the light beam. Usually, a weak magnetic field is used to trap the photodetachment electrons into helical paths around magnetic flux lines transverse to the ion beam, so that the electrons can be separated from the ion beam and accelerated along the field lines into a collector.

An expression for the rate of production of electrons by photodetachment is developed in some generality so that the assumptions used in adapting this formulation to a particular type of measurement can be traced.

The probability \( P_p \) that a negative ion with velocity \( v \) will be photodetached after it enters an illuminated interaction volume at time \( t \) may be written as

\[ P_p(v, t) = (h\nu)^{-1} \int \int W(x, \lambda, t)\sigma_p(\lambda) d\lambda dx, \] (2.3.4)

where \( W(x, \lambda, t) \) represents the radiation flux density at time \( t \) as a function of longitudinal position \( x \) and wavelength \( \lambda \). \( \sigma_p(\lambda) \) is the photodetachment cross section at wavelength \( \lambda \), and \( h\nu/\lambda \) is the energy of a single photon.

The assumptions have already been made that (a) the lateral distribution of radiation flux is uniform across the ion-beam diameter, and (b) the
angular aperture of the ion beam is negligible. The detachment probability is then independent of ion trajectory. The condition for the ion-beam angular aperture, generally fulfilled in practice, is important only for an absolute measurement. The condition of lateral uniformity of the light beam, more difficult to achieve, must be approximately fulfilled for relative measurements as well as for absolute measurements, because the geometry of illumination will vary with wavelength in any light source and imaging system involving refracting elements. Since a detailed measurement of the distribution of ion trajectories has not been feasible, corrections for chromatic aberrations, not always small, can be accurate only if the illumination is approximately uniform over the diameter of the ion beam.

The number of ions photodetached per unit time \( n_p(t) \) is given by

\[
n_p(t) = n_i(t) \int P_p(v, t) f(v, t) \, dv,
\]

(2.3.5)

where \( n_i(t) \) is the total ion (particle) current, and \( f(v, t) \) is the velocity distribution function for the ion beam. Combining Eqs. (2.3.4) and (2.3.5), we obtain

\[
n_p(t) = n_i(t)(hc)^{-1} \left[ \frac{1}{\varepsilon(t)} \right]^{-1} \int_\lambda \left[ \int_\omega W(x, \lambda, t) \, dx \right] \sigma_p(\lambda) \lambda \, d\lambda.
\]

(2.3.6)

The time dependences indicate possible sources of instabilities and fluctuations.

The detailed geometric and radiometric problems associated with absolute and relative measurements were confronted at the National Bureau of Standards in two basic measurements of the cross section for the photodetachment of the negative ion of atomic hydrogen. Branscomb and Smith\(^{19}\) measured the absolute value of the cross section integrated over a broad spectral distribution, providing an experimental check for the normalization of the \( \text{H}^- \) cross section accurate to about \( \pm 10\% \). Smith and Burch\(^{14}\) measured the spectral dependence of the cross section at points from 4000 to 13,000 Å with probable error of \( \pm 2\% \) relative to the value at 5280 Å. This relative measurement has provided a sensitive test for the success of theoretical calculations of the cross sections. It was shown by Geltman\(^{20}\) that highly refined bound-state wave functions and radially correlated free-state wave functions were necessary to achieve near agreement with the experimentally determined energy dependence. The experimental results and Geltman’s calculated cross section are shown in Fig. 2. The calculated data are reproduced in Table I because they provide a reliable means for calibrating a photodetachment apparatus with respect to

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2. PHOTON INTERACTIONS WITH PARTICLES

![Graph showing the cross section for photodetachment of H⁻ calculated by S. Geltman and measured by S. J. Smith and D. S. Burch.](image)


**TABLE I. Cross Section for Photodetachment of H⁻, Calculated by Geltman**

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<th>λ (Å)</th>
<th>σ (10⁻¹⁷ cm²)</th>
<th>λ (Å)</th>
<th>σ (10⁻¹⁷ cm²)</th>
<th>λ (Å)</th>
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* Extrapolated values.

... geometric and radiometric factors: the cross section for a negative ion X⁻ is measured relative to that for H⁻ by using monochromatic photon beams. If we assume 100% collection efficiency and use a suitable correction for the velocity factor, the cross section σ(X⁻) can be determined. The critical assumption in this process is, again, the lateral uniformity of illumination of the ion beams, since it cannot be assumed in general that the H⁻ and X⁻ beams have precisely the same spatial distributions.
Equation (2.3.6) can be simplified for the case of a nearly monochromatic photon beam. For a flux monochromatized at wavelength $\lambda_m$, $W(x, \lambda, t)$ can be approximated by $W(x, \lambda, t)S(\lambda - \lambda_m)$. Here we are including the transmission properties of the monochromator at $\lambda_m$ in the spectral distribution. Then Eq. (2.3.6) for the number of ions photodetached per unit time becomes

$$n_p(\lambda_m, t) = n_i(t)(\lambda_m/\hbar c)[v(t)]^{-1} \sigma_p(X^-, \lambda_m) \int_x W(x, \lambda_m, t) \, dx, \quad (2.3.7)$$

and the cross section can be written as

$$\sigma_p(X^-, \lambda_m) = \frac{n_p(\lambda_m, t)}{n_i(t)} \left[ \frac{\lambda_m}{\hbar c} \left( \frac{1}{v(t)} \right) \int_x W(x, \lambda_m, t) \, dx \right]^{-1}. \quad (2.3.8)$$

If the total optical system, including a radiometer or photosensitive detector that monitors some fraction of the photon beam, is geometrically stable, then

$$(\lambda_m/\hbar c) \int_x W(x, \lambda_m, t) \, dx = [\kappa(\lambda_m)]^{-1} R(\lambda_m, t), \quad (2.3.9)$$

where $R(\lambda_m, t)$ is the response of the radiometer, and $\kappa(\lambda_m)$ is a calibration factor that may be determined through measurement of the known cross section for $H^-$. We have then

$$\sigma(X^-, \lambda_m) = \kappa(\lambda_m) \frac{n_p(\lambda_m, t)}{n_i(t)} \left[ \frac{1}{v(t)} \right] R(\lambda_m, t) \left[ \frac{1}{v(t)} \right]^{-1}. \quad (2.3.10)$$

This relation provides the basis for the recent crossed-beam measurements of photodetachment.

2.3.2.2. Monochromatic Photon Beams. The development of an unusual high-aperture monochromator has been one of the most important recent improvements in photodetachment crossed-beam technique. The instrument, shown schematically in Fig. 3, was designed by A. E. Mann† specifically to meet the requirements of photodetachment measurements. It is characterized by a high effective optical aperture, f/1.5, by a limiting resolution of about 4 Å and by a reciprocal dispersion of about 70 Å/mm when using a 600-line/mm grating. The combination of high aperture and resolution was achieved by the rather drastic step of cutting a hole in the center of a high-quality, 8 × 10-in. grating, so that both the entrance and exit slits could be placed nearly on axis at the focus of the 8-in. f/1.2 parabolic mirror used to collimate the light. A pair of aspheric quartz lenses is used to project the exit beam beyond the housing of the monochromator so that an image of the exit slit can be projected through the

† A. E. Mann, Spectrolab Inc., 12484 Glastone Avenue, Sylmar, California.
window of a vacuum system onto the axis of an ion beam. The position of the image is maintained fixed in space by shifting the longitudinal positions of the final quartz lenses to compensate for longitudinal chromatic aberrations, using a drive mechanism appropriately coupled to the sine-bar grating drive. The slits themselves are 12.7 mm long and open to a maximum of 4 mm with a bilateral adjustment. A beam splitter, a flat sheet of clear quartz, 1 mm thick, is used to split out about 8% of the exit beam for monitoring the beam intensity. The grating is blazed at about 4000 Å to ensure highly effective transmission in an interesting region of the optical spectrum.

The lamp that has generally been used with this instrument is a high-pressure, xenon short-arc lamp operated with a direct-current input power of about 2500 W. Used with an elliptical mirror, about 40 W of radiation are available in the spectral range from 2000 to 14,000 Å within the first field aperture (12.7 × 4 mm) at f/1.5.

2.3.2.3. Photodetachment Probability. From Eq. (2.3.7), the average photodetachment probability can be written as

\[ P_p(\lambda_m) = \frac{i_{pd}(\lambda_m)}{i} = \frac{\lambda_m}{hc} \left( \frac{1}{\nu} \right) \sigma_p(X^-, \lambda_m) \int_x W(x, \lambda_m) \, dx, \]  

(2.3.11)

where \( i_{pd} \) and \( i \) are the photodetachment and ion-beam currents, respectively.
A set of working values of the several experimental parameters is used in the following several sections to illustrate the measurement problem under "typical" conditions. In the typical experiment, it will be assumed that the Mann monochromator, discussed in the previous section, is used with a high-pressure xenon lamp. The lamp output is taken as $10^{-3}$ W/Å/mm slitwidth at the entrance slit of the monochromator. If we take the efficiency of the optical system to be 50% and the reciprocal dispersion as 70 Å/mm, the power in the output beam is $\sim 4 \times 10^{-2} d^2$ or about $10^{17} d^2$ photons/sec in the visible spectrum, where $d$ is the slitwidth in millimeters of the coupled entrance and exit slits.

For an atomic oxygen negative ion of 1 keV, the velocity would be $\sim 1.4 \times 10^6 (eV/M)^{1/2} \sim 10^7$ cm/sec, and the cross section would be $\sim 10^{-17}$ cm$^2$. Here $M$ is in atomic mass units, and $eV$ is the ion energy. For this set of circumstances, the photodetachment probability would be $P_p \sim 10^{-7} d^2$. For an ion-beam current of $10^{-8}$ A, the photodetachment current would be $i_p \sim 10^{-15} d^2$ A.

2.3.2.4. Signal Fluctuations. If the photodetachment current, the ion current, and the radiometer signal could be integrated simultaneously, the statistical uncertainty associated with a measurement of the cross section would be determined by the statistical fluctuations in the integrated photodetachment current. This statistical relative error would be

$$\left[ \frac{(\Delta N_p)^2}{N_p} \right]^{1/2} = \frac{1}{N_p} = \left( \frac{\tau P_p i e}{e} \right)^{-1/2}, \quad \text{(2.3.12)}$$

where $\tau$ is the integrating time, $P_p$ is the photodetachment probability, $i$ is the ion current, $e$ is electronic charge, and $N_p$ is the average number of photodetached electrons received during time $\tau$.

When this result is illustrated with the "typical" oxygen atom situation of the preceding section, the estimated statistical relative error is $\left[ \frac{(\Delta N_p)^2}{N_p} \right]^{1/2} \sim 10^{-3}/(\tau d^2)^{1/2}$. An error $\leq 1\%$ with a 1 mm slit width, corresponding to a half-width of 70 Å, is easy to achieve in principle. However, the contribution to the noise arising from collisional detachment currents has not been taken into account.

Collisional detachment of negative ions is represented by the reaction

$$X^- + M \rightarrow X + M + e, \quad \text{(2.3.13)}$$

where $M$ represents a molecule of the residual gas in the system. When a typical collisional detachment cross section, $\sigma_c \sim 10^{-15}$ cm$^2$, is used, the collisional detachment current per centimeter of ion-beam path is $i_c \sim 20 p i$, where $i$ is the ion-beam current and $p$ is the background gas pressure in Torr. The collisional detachment probability, $P_c = i_c/i \sim 20 p$, is to be compared with $P_p \sim 10^{-7} d^2$, estimated in the previous section for

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the photodetachment probability. The two contributions will be comparable for pressures in the $10^{-8}$ Torr range. If $10^{-10}$ Torr background pressures could be achieved in this type of kinetic-beam experiment, the collisional detachment contribution could be neglected. Direct-current simultaneous integration of photodetachment current, ion current, and radiometer signal would yield a relative value of the cross section with a statistical error determined only by the number of photodetached electrons collected. Fluctuations in ion beam, in background pressure, and in the output of the arc lamp would be taken care of by the averaging process.

However, at practical working pressures of $10^{-7}$ to $10^{-8}$ Torr, the collisional detachment is not negligible, and a technique must be devised for subtracting the collisional from the total detachment signal. The standard technique utilizes a rotating chopper wheel in the photon beam. As a result of light chopping, the photodetachment current is chopped, whereas the collisional detachment current is not. The difference current, appearing ideally as a square wave equal to the photodetachment current, is detected synchronously and integrated for time $\tau$. The purely statistical fluctuation due to the discreteness in the integrated current is simply the statistical fluctuation in the integrated total detachment current: the square root of the total number of detached electrons arriving during the integration time $\tau$. Thus, if the collisional detachment probability is very large compared to the photodetachment probability, the statistical fluctuation problem is correspondingly more serious.

Gross fluctuations in the ion-beam current and in the background gas density and composition introduce further complications in the analysis of integrated signal fluctuations through the gross fluctuations transmitted to the total detachment currents and to the collisional detachment current, respectively. Fluctuations in the envelopes of the ion current and background gas density are equivalent to fluctuations in the detachment probabilities, and are independent of fluctuations due to the discrete nature of the currents involved. The Fourier components near the chopping frequency degrade the accuracy of the subtraction of collisional from total detachment signals. Little is known about the frequency spectra or about the amplitudes of such fluctuations. These certainly vary from instrument to instrument and depend on a number of loosely controlled or little-understood factors.

It should be noted that fluctuations in background pressure can be minimized through proper vacuum engineering. In particular, the pressure-fluctuation time constant, the volume divided by the molecular conductance to the fluctuation sources (vacuum pumps), may be maximized, but at the cost of pumping speed, with a fixed volume. Alternatively, the volume can be increased in order to achieve a larger time constant (see Section 1.3).
2.3. PHOTODETACHMENT

The fluctuations in the effective detachment probability can be assumed to be noncoherent on the time scale of a typical integration, so that relative fluctuations in observed detachment probability from this cause vary inversely as the square root of integrating time. For purposes of illustrating the restrictions such fluctuations impose on measurements, we shall assume that the amplitude of the noise is proportional to the magnitude of the ion current, which may or may not be the case in a particular circumstance.

Therefore, we represent the relative fluctuations in the ion-beam current as a large factor \( F \) times the relative shot noise predicted for an ion-beam current \( i_P \):

\[
\frac{(i_n^2)^{1/2}}{i} = \frac{(i - i)^{1/2}}{i} = F \left( \frac{e}{i_P \tau} \right)^{1/2},
\]

valid only for \( F \gg 1 \). The ion current \( i_P \) may be any current at which \( F \) is evaluated. The noise characteristics of negative ion beams have been studied by Fite. Typically, the root mean square noise in an ion beam of about 10\(^{-8} \) A is several orders of magnitude larger than the predicted shot noise within a five-cycle bandwidth \( B \), where \( \tau \) is equivalent to \( 1/2B \sim 1/20 \) sec of integration. Then \( (i_n^2)^{1/2}/\bar{i} = 4 \times 10^{-6}F/\tau^{1/2} \). This relative fluctuation will appear in the detachment currents derived from the ion beam, superposed on the "shot" noise.

Pressure fluctuations will result in corresponding fluctuations in the collisional detachment current \( i_c \). Since \( i_c \sim 20pi \), where \( p \) is background pressure in Torr and \( i \) is ion-beam current, we can write

\[
[(\bar{i}_c - \bar{i}_c^2)]^{1/2} = 20i[(\bar{p} - \bar{p})^2]^{1/2} \quad \text{or} \quad [(\bar{i}_c - \bar{i}_c^2)]^{1/2}/\bar{i}_c = [(\bar{p} - \bar{p})^2]^{1/2}/\bar{p}.
\]

The fluctuations in \( i_c \) due to fluctuations in \( p \) are proportional to the ion-beam current. Thus, pressure fluctuations have exactly the same effect as would the same relative fluctuation occurring in the ion beam, except that the photodetachment current is not affected by pressure fluctuations.

When we take into account that the photodetachment current is a chopped current, whereas the collisionally detached current is not, the net fluctuation in total detachment current integrated for time \( \tau \) may be represented as

\[
(i_n^2)^{1/2} = \left[ F^2 \bar{i}_P \left( 2\tau \right)^{-1/2} \left( \bar{i}_c^2 + \bar{i}_p^2 + \bar{i}_c^2 \right) \right]^{1/2} + \left[ (\bar{p} - \bar{p})^2 / \tau_0^2 \right]^{1/2} \bar{i}_c + \left( e \bar{p}/2\tau \right)^{1/2},
\]

where \( i_c \) and \( i_p \) are instantaneous collisional and photodetachment currents.

\[\text{W. L. Fite, Ph.D. Dissertation, Harvard University (1951).}\]
The quantity $\bar{i}_p$ is taken as the average of $i_p$ over the half of the integrating time during which photodetachment takes place. The relative error in a photodetachment measurement may be written as

$$\frac{(\Delta(N_e + N_p)^2)^{1/2}}{N_p} = \frac{2(i_e^3)^{1/2}}{i_p}$$

$$= \frac{2P^2_P}{i_e i_p} \left[ \left( \frac{P_e}{P_p} + 1 \right)^2 + \left( \frac{P_e}{P_p} \right)^2 \right]$$

$$+ 4\left( \frac{(\bar{P} - P_e)^2}{P_e^2} \right) \left( \frac{P_c}{P_p} \right)^2 + \frac{4e}{(P_e i_p)^2} \left( \frac{P_e}{P_p} + 1 \right)^{1/2}$$

(2.3.16)

in terms of the photodetachment probability $P_p$, the collisional detachment probability $P_c$, and the ion current $i_p$.

Figure 4, based on Eq. (2.3.16), illustrates the signal-to-noise problem as it is limited by fluctuations in the detachment current. The effects of fluctuations in background pressure are not included. The theoretical signal-to-noise ratio, for a 1-sec integration, is plotted against the ratio of the probabilities $P_c$ and $P_p$ for collisional detachment and photodetachment of an ion, for various photodetachment currents $i_p$.

Fig. 4. Signal-to-noise ratio (multiplied by the inverse square root of the integrating time) is plotted against the ratio of the probabilities $P_c$ and $P_p$ for collisional detachment and photodetachment of an ion, for various photodetachment currents $i_p$.

In general, as this ratio grows larger, the signal-to-noise ratio deteriorates because of the increasing importance of the noise carried by the collisionally detached electrons.
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The two heavy curves indicate the role played by the ion-beam "flicker," which dominates when the photodetachment current is large if $F \gg 1$. The two curves illustrate the particular cases of noise levels $F = 100$ and $F = 1000$ times shot noise within a one-half cycle bandwidth in a $10^{-8}$-A ion beam. The upper curve, for $F = 100$, is probably more nearly typical than the lower curve ($F = 1000$) for such a narrow bandwidth.

Below the appropriate "flicker" curve, the signal-to-noise ratio is determined by the particle statistics, the "shot" noise, in the total detachment current. In this region, $(S/N)_{T}^{-1/2}$ is shown by the lighter curves, each one corresponding to a given value of the photodetachment current. These are plotted taking $F^{2}/i_{p} = 10^{14}$. At the extreme left side (at very low pressure or for very high light flux), where collisional detachment is neglected, the curves tend toward constant values.

The transition from shot-noise domination to flicker domination at fixed values of $P_{e}/P_{p}$ occurs rather abruptly, within a decade in the ion current or photodetachment current. The signal-to-noise ratio saturates rather abruptly, and larger ion currents are not helpful, unless accompanied by significant improvements in $P_{e}/P_{p}$.

The ratio $P_{e}/P_{p}$ expresses the role of the ratio of background pressure to light flux. $P_{p}$ is represented generally by Eq. (2.3.11) and, for the particular case of the Mann monochromator, by the expression $P_{p} \sim 10^{10} \sigma_{p} d^{2}$. $P_{e}$ is well represented by the expression $P_{e} \sim 20p$ (Torr). In general, this ratio can be written as

$$P_{e}/P_{p} = \frac{\bar{i}_{e}/\bar{i}_{p}}{2 \times 10^{16} \sigma_{e} \rho(hc/\lambda_{m})(1/e)^{-1} / \alpha_{p} \int W(X, \lambda_{m}) \, dx.} \quad (2.3.17)$$

This is $P_{e}/P_{p} \sim 2 \times 10^{9} p/d^{2}$ for the Mann monochromator. Here $\rho$ is background pressure in Torr, and $d$ is slit width in millimeters corresponding to a triangular optical band-pass about 140Å wide at the base.

It is clear from Fig. 4 that the most significant design parameter is the photodetachment probability, since this improves the ratio $P_{e}/P_{p}$ and, in the shot-noise region, increases the photodetachment current $i_{p}$. Thus, the development of the high-aperture monochromator was a major step forward. The next step is likely to be the further application of high-output lasers to the photodetachment problem.

For a given light flux, the significant parameter is background pressure. Improvements in pressure are rewarded by significant improvement in signal-to-noise ratio for $P_{e}/P_{p} \gtrsim 1$. Clearly, pressures of the order of $10^{-8}$ Torr and lower are desirable for high-resolution work, so that high-quality vacuum design and instrumentation are essential.

2.3.2.5. Measurement of Detachment Current. In early photodetachment measurements, the chopped detachment current was collected on an
electrode that was directly connected to the grid circuit of a high-impedance, low-noise preamplifier. In a battery-powered preamplifier developed by Smith, the first stage of a grounded-cathode, grounded-grid cascode amplifier was placed inside the vacuum housing to reduce input capacitance to about 5 pf. This preamplifier is shown schematically in Fig. 5. Since the

![Schematic diagram of a low-level cascode preamplifier designed for measurement of photodetachment current.](image)

photodetachment current generates a signal voltage $S \approx i_p X_c$, where $X_c = (\omega C)^{-1}$, and since the Johnson noise at the grid due to the input resistor $R$ is $N_R \approx (X_c/R) \times (4kTRB)^{1/2}$, the signal-to-noise ratio is proportional to $R^{1/2}$. A resistance of $R \approx 2 \times 10^{10} \Omega$ was chosen to optimize the signal-to-noise ratio within the limits imposed by the tube noise. Reduced heater currents and plate currents minimized the tube noise. A feedback loop was used to keep the preamplifier near the center of the operating range, despite the effect of direct-current components of the detachment current. The gain of this preamplifier was of the order of 25. The direct-current characteristic curve is shown in Fig. 6.

The resistor noise current can be estimated to be $N_R \approx 1.3 \times 10^{-15}/\tau^{1/2}$ at the input. For $\tau \approx 100$ sec, this is comparable to or slightly smaller than the magnitude of the current predicted from a $10^{-8}$-A ion beam.

when 140 Å resolution is used. Therefore, this preamplifier has been used generally for lower resolution measurements and for ions that can be produced in larger currents. This preamplifier has been most useful for the basic work on $\text{H}^-$, where the absolute value and relative cross section were determined accurately, but with very low resolution.

For the high-resolution work, the open secondary-emission multiplier with gains of $\sim 10^4-10^6$ is essential. In high vacuum, a well-constructed multiplier can be noise-free except for occasional pulses resulting from radioactivity and cosmic-ray background. This method was first applied by Semen and Branscomb$^{11}$ to the determination of the electron affinity and cross section of atomic carbon; it has been used in all subsequent work with high-resolution monochromators. The noise levels that can be achieved are mainly due to particle statistics as discussed in the previous section, since these noise sources will normally swamp the dark current in any reasonably good multiplier.

The limitations of this system are associated with collection efficiency and geometric stability of the electron optical system. Semen and Branscomb used a weak magnetic field to trap the detached electrons, a weak electric field to extract them, and electrostatic lenses to focus them onto the first
dynode of the multiplier. Subsequently, Hall et al.\textsuperscript{24} showed that the optimum collection efficiency of this particular system is only \(\sim 15\%\). This might be expected to vary with the wavelength of the photons (e.g., with the ejected electron energy). The calibration of this system by reference to the cross section for photodetachment of \(\text{H}^-\) becomes complicated because of possible differences in collection efficiency between \(\text{H}^-\) and other negative ions with different binding energies. For an accurate determination of the radiometric factor, \(\text{H}^-\) could be studied with an auxiliary collection system for which the collection efficiency is 100\%.

Subsequently, the effects of variation of collection efficiency with electron energy could be determined using \(\text{H}^-\) in the less efficient system. Within a limited energy range, and where more qualitative features are of interest, the procedure can be simplified to a direct calibration with \(\text{H}^-\).

Steiner\textsuperscript{25} has noted that the efficiency of the open cascade-type multiplier is highly variable as a function of position of electron impact on the first dynode. His collection geometry, unique in that it is a purely electrostatic system, is shown in Fig. 7. This system can also be calibrated by

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\textsuperscript{25} B. Steiner, private communication (1966).
reference to the H− cross section. In multiplier systems, the requirement for geometrical stability of the electron and ion optics is likely to be a limiting factor in the quality of the results which can be achieved.

2.3.2.6. The Crossed-Beam Photodetachment Apparatus. The crossed-beam photodetachment apparatus most recently developed was designed and built by Steiner at the National Bureau of Standards. Steiner has undertaken to extend the photodetachment technique to the study of a wide range of molecular negative ions. The major objective in his design is to obtain an optimum combination of high-mass resolution and high ion-beam transmission.

His instrument is shown schematically in Fig. 8, and Fig. 9 is a photograph of this instrument with the electrostatic ion-beam analyzer omitted.

![Diagram](image)

**Fig. 8.** Schematic diagram of Steiner’s photodetachment apparatus.

The ion optics, more sophisticated than any previously used in photodetachment work, is designed for high resolution through use of large radii and carefully designed second-order corrections. The double-focusing feature results in first- and second-order e/m resolution, independent of ion-energy spread or of differences in mean ion velocity from one species
to another. This is a necessary feature for the separation of adjacent mass numbers at high masses, since energy spreads arising in ion sources are typically 25–50 eV at half-peak height. The analyzer is operated at 2.5 keV and is designed for a mass resolution of the order of unity at mass 150. Energy spreads of magnitudes $\Delta V = (\Delta M/M)V \sim 25$ eV will begin to degrade the mass separation. It is essential to have pure ion beams at the interaction region, since a small intrusion of an ion having a large photodetachment cross section can result in an erroneous measurement.

Figure 10 is a schematic diagram of a hot-cathode arc used by Branscomb and his collaborators to produce their negative ions. The cathode is a 20-mil wolfram wire. Arc pressures are empirically determined and may vary from a few microns up to 100 $\mu$. The voltage drop may be about 50 V, with a total arc current of a few hundred milliamperes. Four electrically floating stainless-steel disks are used to confine the discharge to the axis of the tube, using apertures ranging from 5 mm at the cathode to 1 mm at the anode. A weak magnetic field has been used to help confine the arc, but this is not used in Steiner's version.
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Fig. 10. Schematic diagram of the hot-cathode arc source used by Branscomb and collaborators.

This arc is now the most commonly used source of negative ions for photodetachment experiments. It has been used with a number of source gases. The spectrum of negative ions from a discharge in carbon monoxide is shown in Fig. 11. Discharges in ammonia yield high currents of H\(^-\) as well as heavier masses. Ammonia has been used with traces of other gases such as H\(_2\)O and O\(_2\) to produce oxygen and hydroxyl ions. Steiner has used a mixture of ammonia and sulfur hexafluoride for a beam of SH\(^-\) ions. Discharges in pure oxygen yield O\(^-\) and O\(_2\)\(^-\) ions, but the lifetime of the filament is limited in this situation. The use of ammonia as a carrier provides a reducing atmosphere and prolongs filament life.

2.3.3. Laser Photodetachment of I

In one of the most spectacular recent applications of lasers, Hall et al.\(^{24}\) have observed and measured the photodetachment of I\(^-\) by 1.785-eV photons. Since I\(^-\) has only one bound state at \(-3.076\) eV, the photodetachment signal observed was necessarily due to the simultaneous absorption of two photons.

The photon beam was produced by a 20-MW, Q-switched ruby laser. The experimental arrangement is represented in Fig. 12. The laser light was produced outside the vacuum apparatus and focused through a window into the ion beam by conventional f/8 optics. After passing through the ion beam, the light was reflected at a 90° angle by a
Fig. 11. Mass spectrum of negative ions obtained from a discharge in CO. The two traces are high and low amplifier gains.

front-silvered mirror, through a vacuum window onto a magnesium-oxide coated screen external to the vacuum system. The screen was viewed by a high-speed biplanar photodiode, and the output signal of the diode was displayed using a traveling-wave oscilloscope.

The integrated response of the photodiode was calibrated in an auxiliary measurement of the energy in a laser pulse, using a liquid-cell calorimeter containing a solution of copper sulfate. The laser beam was simultaneously monitored with a secondary photodiode that received light split out from the primary beam by a plane unsilvered sheet of glass. Then, with the
calorimeter effectively replaced by the MgO sheet and the primary photodiode, the calibration was transferred from the secondary to the primary photodiode.

No special precautions were used in the selection of optical elements, although it was necessary to show that there was no generation of second-harmonic photons of 3.56-eV photons which could produce photodetachment in a one-photon process.

The laser beam actually passed through its focus before it intersected the ion beam and was spread out to a diameter of about 1 mm at the ion beam. Since the two-photon process is proportional to $F^2$, the square of the flux, it is desirable to keep the flux concentrated to get a large signal. However, if the photon flux density is so high that the ion density changes appreciably during the laser pulse, then the photodetachment response is erroneously low.

A serious limitation on the measurement was the result of inherent difficulties in determining the overlap between the ion and photon beams. The spatial distributions were studied by photographing phosphor screens on which the ion and photon beams (at low laser power) were incident. The ion-beam diameter was found to be about 4 mm, and this was used to estimate average ion density.

The photon-beam diameter was easily varied from a lower usable limit of about 1 mm up to 4 mm by moving the position of the focus. Since the
ruby laser does not operate with uniform efficiency and coherence over its entire cross section, but is divided into a number of bright coherence zones or modes, the illumination in the diverging light beam at the position of the ion beam varies from one element of solid angle to another. There are, in effect, a number of beams emerging from the focus, so that illumination of the ion beam will be patchy, with the patches at least partially separated. The patchiness results in an increase in the effective value of $F^2$ over that of a single mode uniformly filling the optical aperture. Hall et al. made estimates of these effects and concluded that they could evaluate the effective $F^2$ to an accuracy of about 50%.

The photodetached electrons were collected by the optical system shown in Fig. 12 and accelerated into a multiplier. The weak magnetic field $H_0$ served to trap the electrons into helical orbits along the field lines. The electrons were weakly accelerated downward out of the interaction region and then strongly accelerated and focused into a multiplier. The response of the multiplier to a single electron was determined by studying the pulse height distribution of single collisionally detached electrons. The electron-collection efficiency was determined by photodetaching a beam of $H^-$ ions with the photon beam from the $Q$-switched laser. Full power of 20 MW corresponds to a flux of $10^{27}$ photons/cm$^2$-sec. The photodetachment cross section is $\sim 10^{-17}$ cm$^2$, and the transit time is $\sim 10$ nsec in the photon beam. The pulse duration is of the order of 50 nsec. Since a $H^-$ ion of 500 eV traverses the photon beam in approximately 10 nsec, the photodetachment process is fully saturated, and the rate of production of photodetached electron current is known. The collection efficiency was determined to be one-seventh.

Hall, Robinson, and Branscomb were able to show that the two-photon process in $I^-$ has a transition probability per second of $W_2 = 2.7 \times 10^{-49}$ cm$^4$-sec $F^2$, where $F$ is the photon flux density in photons-cm$^{-2}$-sec$^{-1}$, and the estimated uncertainty in the numerical coefficient is 50%. The additional coherence corrections that were applied in the paper are now believed not to be necessary.

A comparison of the experimental results with theory has been carried out by Robinson and Geltman.$^{28}$

2.3.4. Photodetachment in a Drift Tube

Woo and Beaty$^{27}$ have made the first observations of photodetachment of molecular negative ions in equilibrium with the parent gas. This preliminary success is particularly significant in view of the ambiguity of crossed-beam experiments with respect to the distribution in states of the molecular negative ions. In the drift-tube experiments, the system is at least


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characterized by ambient pressures, temperatures, and gas composition. These can be related to typical atmospheric conditions, for example.

Woo and Beatty used a drift tube designed for the study of ionic mobilities. The entire tube was at one pressure. In the present work, \( p \approx 10 \) Torr of oxygen gas. Ions were produced in a cold-cathode discharge, and gated into a 10-cm-long drift space of about 2.5 cm diam. The tube was operated at \( E/p \approx 2 \) V/cm-Torr, which corresponds to a drift velocity of \( \sim 3 \times 10^3 \) cm/sec. Since the drift velocity is much less than thermal velocity, the condition of thermal equilibrium is not violated.

The source gate, a pair of parallel grids, was opened for 300 \( \mu \)sec to admit a pulse of negative ions. About \( 6 \times 10^8 \) ions per pulse arrived at the collector end of the drift space, within a span of time which is somewhat larger than 300 \( \mu \)sec because of diffusion and space-charge effects.

A 2-kW, high-pressure xenon arc lamp was used to illuminate at \( f/1.5 \) a cross-sectional area 3 \( \times \) 3 cm in front of the collector. Light from the xenon lamp was collected by a 13-in. spherical mirror and focused into a 60-cycle chopper wheel at a distance of 26 in. The light diverging from the chopper was focused into the drift tube by a 4-in. glass lens at \( f/1.5 \). The power available at the drift tube was about 40 W, or 4.4 W/cm\(^2\), as determined from simple calorimetry. The full unfiltered power was used to obtain a detectable signal.

The collector gate could be operated as an electron filter so that the signal current consisted of photodetached electrons. This was accomplished by applying a 14-V peak-to-peak 100-kc square wave to the gate. This led to collection of about 50\% of the electrons that appear at the gate, but because of the longer transit time the negative ions cannot pass. The gate was opened to electrons periodically in this manner at a rate of 60 cps, each cycle consisting of 800 \( \mu \)sec open time and closed the remainder of the time. The gate could be operated synchronously with the chopped light signal. A signal corresponding to about \( 1.5 \times 10^3 \) electrons per pulse was observed. This is of the order of magnitude predicted on the basis of the cross section as measured in beam experiments and on the basis of approximate information as to the intensity and spectral distribution of the light. Antisynchronous operation yielded no signal.

The analysis, not yet completed, is complicated by questions of collection efficiency and reattachment rates, but the method seems certain to yield valuable information.

2.3.5. The Shock-Tube Method

Berry and collaborators\(^{28,29}\) have studied the structure of negative halogen ions in an ingenious series of photographic measurements of the


attenuation of light transmitted through a shock-heated gas. The experimental arrangement is illustrated in Fig. 13.

The shock was initiated by the bursting of a scribed aluminum diaphragm between the high-pressure driver section 5 ft long and a low-pressure section 15 ft long. The bursting pressure and the strength of the shock were controlled by the depth of the scribe marks on the diaphragm. Hydrogen was used in the driver section at final pressures from 200 to 350 psi. The low-pressure gas was argon at 1.5 to 2.5 cm Hg. Shock velocities were of the order of Mach 9.

Alkali halide salts were supported on tissue paper or on thin perforated aluminum foil at a point 90 cm from the optical absorption path. The salts were volatilized at the temperature prevailing behind the shock front and carried along behind the shock in approximately equilibrium concentrations of molecules, atoms, positive ions, and negative ions. Typical gas densities behind the shock front were $6 \times 10^{17}$ atoms/cm$^3$ or greater.

By using the reaction $\text{CsI} \rightarrow \text{Cs}^+ + \text{I}^-$ as an example, it can be shown from the law of mass action that

$$N(I^-)N(Cs^+)/N(CsI) = 5 \times 10^{23} T^{-1/2} \exp(-\epsilon_0/T), \quad (2.3.18)$$

where $\epsilon_0$ is the energy per molecule ($\sim 4.2$ eV) required in the reaction. The numerical coefficient is determined by rotational and vibrational constants of CsI and by the masses of Cs, I, and CsI. This coefficient does not vary enormously from one alkali halide to another.

Furthermore, for the reaction $\text{CsI} \rightarrow \text{Cs} + \text{I}$, the same numerical
coefficient is valid. A factor $g = 8$ must be inserted for the statistical weights of I and Cs (confining our attention to the $J = \frac{1}{2}$ state of I), and the dissociation energy of CsI ($\sim 3.4$ eV) must be used for $e_0$.

From these considerations, it is easy to see that the alkali halide salts are very highly dissociated at 3000° to 4000°K, and that the ratio

$$N(Cs)N(I)/N(Cs^+)N(I^-) = 8^{e_2.1} \sim 175 \quad \text{at} \quad 3000°K,$$

$$= 8^{e_2.3} \sim 80 \quad \text{at} \quad 4000°K.$$  

In the absence of free electrons, $N(Cs) = N(I)$ and $N(Cs^+) = N(I^-)$. In this case, $N(I)/N(I^-) \sim 13$ at 3000°K and $\sim 9$ at 4000°K. As the temperature rises through this range, the Saha equation indicates an increasingly significant free-electron density at the expense of the negative-ion population.

Berry et al. showed that salt concentrations of $\sim 10^{17}$ molecules/cm$^3$ would lead to negative-ion concentrations of $10^{15}$ to $5 \times 10^{15}$ ions/cm$^3$ at 3000° and 4000°K, respectively. Therefore, with typical cross sections of $10^{-17}$ cm$^2$ for photodetachment, they predicted optical depths equal to unity for optical paths of 100 and 20 cm, respectively. Indeed, Berry found that, by using the four-pass multiple-reflection system described by White,30 which gave him a 34-cm absorption path, he could see sharp absorption edges due to photodetachment of halogen negative ions.

The light source was a fused-silica, capillary flash lamp, which used continuously pumped air at about 1 Torr pressure. A 3.3-$\mu$F capacitor bank charged to 11 kV was discharged through the lamp in about 25 $\mu$sec to illuminate the gas immediately behind the shock. The spectrum of the transmitted light was recorded using a conventional prism spectrograph. A microdensitometer tracing is shown in Fig. 14 showing the absorption edge for Cl$^-$.  

The negative-ion absorption was seen against a background of Stark-broadened lines of iron, aluminum, and alkali atoms. The nature of these lines was dependent on the type of base used to support the salt, the choice of salt, and the intensity of the shock. Some molecular-band systems were seen if cleansing tissue was used as a supporting structure or if the alkali halide salt was not completely dry. The choice of salt depended largely on the effect of alkali lines in obscuring the negative-ion continua. F$^-$ was studied by using potassium fluoride. Cesium, rubidium, and sodium salts were used to study I$^-$, and cesium and rubidium salts were used for Br$^-$ and Cl$^-$.  

The locations of the negative-ion absorption edges were predictable from approximate values of the electron affinities available in the literature.

Fig. 14. Microdensitometer tracing showing the absorption edges due to photodetachment of Cl\(^-\) in a shock-heated gas. The comparison trace shows the absorption obtained when the CaCl salt is omitted.

Three other major characteristics were used to obtain positive identification:

1. Since the photodetachment process for a halogen negative ion corresponds to the removal of a p-orbital electron to an s-continuum orbital, the photodetachment cross section should rise as the square root of the excess energy. The observed absorption edge should be quite sharp at threshold.

2. The photodetachment process leaves the halogen atom in either a \( ^2P_{3/2} \) or a \( ^2P_{1/2} \) level, so that there should be two distinct absorption edges with the appropriate separation.

3. The relative intensities of the two absorption steps corresponding to final \( P_{3/2} \) and \( P_{1/2} \) states should be in the ratio of the statistical weights, assuming there is \( L-S \) coupling. The observed absorption edges had these characteristics, and identification could be considered positive.
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The spectral resolution of the optics used was typically $\pm \frac{1}{2}$ Å. Berry et al. were able to put upper limits of $\pm 2$ or 3 Å on the error in their assignment of threshold values. The assignment of the fluorine threshold value was somewhat less accurate than the others because the stronger shocks required to dissociate the fluoride salts intensified the interfering line structure.

Berry et al. studied the shapes of the cross sections near threshold. The plates were calibrated using seven-step neutral-density filters. On the basis of estimates of ion densities and assuming approximate thermodynamic equilibrium, they were able to assign rough values for the magnitudes of the cross sections for photodetachment. Effects of absorption by constituents of the shock other than negative ions were studied by taking spectra of shocks which included the supporting structures of tissue or aluminum but which omitted the salts. This sort of analysis is of somewhat limited value, since much of the energy in the shock is consumed in the vaporization and dissociation of the salts, and the characteristics of the shock are drastically affected. The authors observed that the shock temperature was about 8000° ahead of the sample and that it fell to about 3000° behind the sample.

The shock-tube method of doing photodetachment has proved to be a valuable tool, and the results complement the beam work quite well. One aspect of the shock-tube work of greatest interest has been the question of Stark-broadening and shifting of levels and how these might affect the determination of electron affinities. Berry and Reimann concluded that shifts are small compared to the spectral resolution of their experiment. Some threshold broadening is observed. The toes of the absorption curves are more sensitive to variations in shock conditions than the position of thresholds extrapolated from the rising part of the absorption curves.

The crossed-beam and shock-tube data are generally consistent, which indicates that plasma effects are not serious. Aside from such effects, the shock-tube method has some advantage in spectral resolution and in the convenience of examining the behavior of a cross section near threshold. Berry et al. have discussed in great detail the application of shock-tube data to the study of threshold shapes of Cl$^-$, Br$^-$, and I$^-$ photodetachment curves.

2.3.6. Radiative Attachment Studies of Atomic Negative Ions

The radiative attachment reaction of Eq. (2.3.2)

$$X + e \rightarrow X^- + h\nu$$

is the reverse of the photodetachment process, and the cross sections $\sigma_{\text{at}}$ and $\sigma_d$ for radiative attachment and photodetachment are related through the principle of detailed balancing:

$$
\sigma_{\text{at}}(X) = \frac{g(X)}{g(X^-)} \frac{h_\nu^2}{m^2c^2 \sigma_d(X^-)},
$$

(2.3.19)

where $h\nu$ is the photon energy, $m$ is electron mass, $c$ is electron velocity, $c$ is the velocity of light, and $g(X)$ and $g(X^-)$ are the statistical weights of the atom and negative ion. Since the atomic negative ion is usually assumed to have only one bound state, measurements of radiative attachment to atoms can be unambiguously related to the photodetachment cross section. In principle, then, detailed studies of radiative attachment are exactly equivalent to measurements of the photodetachment cross section, and it is important to mention examples of radiative attachment measurements to complete the discussion of photodetachment methods.

All work of this type has been carried out in high-temperature devices such as arcs and shock tubes. In 1951, Lochte-Holtgreven\textsuperscript{4} observed an emission continuum from a wall-stabilized hydrogen arc which he attributed to radiative attachment of electrons to atomic hydrogen. In 1958, Weber\textsuperscript{32} published studies of emission spectra from a hydrogen shock tube, and Boldt has studied the continuous emission from radiative attachment of electrons to oxygen atoms\textsuperscript{33} in an arc. Boldt also observed an affinity spectrum in nitrogen,\textsuperscript{34} possibly due to attachment to metastable nitrogen atoms. These measurements were carried out at relatively high temperatures (>10,000°) in order to obtain the high electron densities needed. At these temperatures, free-free transitions are an important source of continuum, and the analysis of the contribution from radiative attachment becomes difficult to accomplish with precision.

Berry and his collaborators, working with shock-heated gases at lower temperatures, have observed emission edges due to radiative attachment to Cl, Br, and I. This observation confirms their earlier absorption measurements described in the preceding section. More recently, Berry et al.\textsuperscript{35} have carried out an elaborate analysis of the threshold region of the continuum from attachment to atomic oxygen. In this work, they were able to determine the electron affinity of oxygen with great precision (1.478 ± 0.002 eV) and to make the first determination of the separation of the $^2P_{1/2}$ and $^2P_{3/2}$ states of O\textsuperscript{−} (285 ± 15 cm\textsuperscript{-1}).

The key to their success was the use of compounds of the alkali metals, as in the shock-tube photodetachment work described in Section 2.3.5. In the case of radiative attachment to atomic oxygen, shocks in neon or argon were loaded with potassium peroxide or rubidium oxide. The alkalis, because of their low ionization potentials, are good electron sources. At shock-tube temperatures of 3000° and 4000°, the alkalis are highly ionized. The equilibrium ratio of atoms and negative ions, in the presence of a plentiful supply of electrons, is governed by the Boltzmann factor containing the electron affinity $e_A$. Higher electron affinities lead to higher negative-ion densities. In the case of the halogens, with electron affinities of the order of 3 eV, Berry and collaborators were able to obtain the densities of $10^{15}$ ions/cm$^3$ at 3000°K, as is necessary to carry out absorption measurements; but, with atoms of lower electron affinities, these densities cannot be reached. For example, the Boltzmann factor for atomic oxygen is $e^6 \sim 150$ times smaller than for iodine.

Using the radiative attachment coefficient determined by Branscomb and Smith from crossed-beam photodetachment data and using the estimates of the atomic oxygen and electron concentrations based on the assumption of thermodynamic equilibrium, Berry et al. predicted a photon emission at 4000°K due to radiative attachment of $10^{11}$ quanta/cm$^3$/sec/wave number, near threshold. These temperatures were achieved in reflected shocks. The observations were made using an $f/4$ spectrograph with a resolution of 28 Å/mm. An estimated $10^4$ photons were incident on a slit image on the film. Microdensitometer traces could be made of the spectrum observed at a fixed time during the shock. Impurity lines permitted accurate calibration of the wavelength scale.

Since the threshold for detachment of a $p$-orbital electron rises abruptly, approximately as the square root of the energy of the outgoing photodetached electrons, these thresholds can be identified with small discontinuities in the microdensitometer trace of the continuum in regions free of line spectra. Identifications of the several thresholds must be consistent with the known separations of the $3P_{0,1,2}$ states of atomic oxygen and with a reasonable value of the $O^{-}(2P_{3/2})$ and $O^{-}(2P_{1/2})$ state separation. Berry et al. were able unambiguously to identify thresholds at 8592 ± 6 Å, 8382 ± 6 Å, and 8776 Å on the basis of 17 observations taken under various conditions. The separation between the last two of these was identified with the $O(3P_2) - O(2P_1)$ separation from known spectroscopic data. The thresholds were identified with the transitions:

$$O(3P_2) + e \rightarrow O^{-}(2P_{1/2}), \quad (2.3.20a)$$
$$O(3P_2) + e \rightarrow O^{-}(2P_{3/2}), \quad (2.3.20b)$$
$$O(3P_1) + e \rightarrow O^{-}(2P_{3/2}). \quad (2.3.20c)$$
On the basis of this assignment, precise values of the electron affinity of atomic oxygen and of the fine structure of the negative oxygen ion were determined.

2.4. Ionization, Detachment, and Dissociation by Electric and Magnetic Fields*

2.4.1. Introduction

An electron in an atomic system is bound by the coulomb attraction of the positively charged nucleus. If a sufficiently great electric field is applied to the system, the binding force can be overcome and an electron completely removed. By looking, for example, at the potential energy of the electron in hydrogen-like systems in strong electric fields, it can be seen that the atomic center is not the only place at which the potential is a minimum; at distances that are sufficiently far from the atom in the negative field direction, the potential is even lower. Now it is well known in wave mechanics that whenever two potential troughs exist it is always possible for the electron to pass from one to the other; if the electron is initially in the atom, it can tunnel through the barrier to the outer region, and the atom becomes ionized. Furthermore, if the electric field is increasing in time, it is possible that the rate of increase is such (see Section 2.4.2.1) that the potential barrier disappears before tunneling can occur, and the electron is then detached directly. The field ionization of hydrogen atoms was first observed by Rausch von Traubenberg et al.\(^1\) during the study of the Stark effect in the Balmer spectrum. The time scale of the experiment was such that barrier penetration could occur, and ionization was observed at field strengths much below those required for direct detachment.

In the case of molecular systems, an applied field perturbs the electron motion and thereby perturbs the potential seen by the nuclei. In certain cases (see Section 2.4.2.2), a potential barrier is formed through which one of the components of the molecule can escape. Dissociation may then take place at lower field strengths than are needed for ionization.

This property of an electric field which enables an electron to be removed or a molecule to be dissociated has been used to study the formation of


* Chapter 2.4. is by A. C. Riviere.